

Tracking mercury from the mine to the power plant: geochemistry of the Manchester coal bed, Clay County, Kentucky

Tanaporn Sakulpitakphon^{a,b}, James C. Hower^{b,*}, William H. Schram^b, Colin R. Ward^c

^aDepartment of Geological Sciences, University of Kentucky, Lexington, KY 40506, USA

^bCenter for Applied Energy Research, University of Kentucky, 2540 Research Park Drive, Lexington, KY 40511-8433, USA

^cSchool of Geology, University of New South Wales, Sydney, NSW 2052, Australia

Received 14 March 2001; received in revised form 29 September 2003; accepted 30 September 2003

Abstract

The high volatile A bituminous Manchester coal bed was sampled at five mine sites in central Clay County, southeastern Kentucky. The coal bed has a high mercury concentration at certain sites, particularly in the high-sulfur uppermost lithology. Whole-coal Hg contents range up to 0.52 ppm in a sample with 3.36% pyritic sulfur. Hg is enriched in the upper lithotype at several of the sites. Arsenic content exceeds 700 ppm (ash basis) for all of the whole channel samples and exceeds 1000 ppm for several of the lithotype samples.

Regional geochemical trends, from an area of approximately 75 × 60 km, were determined using data from this study in combination with data published by the U.S. Geological Survey. Hg, As, Pb, and Cl contents exhibit highs in the northwestern portion of the region. Within the smaller area covered by the detailed mine study, the two western sites both have a high-sulfur upper lithotype containing high levels of As and Hg. Basement structures, previously described in the study area, could have influenced the regional coal rank and geochemistry, possibly acting as conduits for mineralizing fluids.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Kentucky; Coal; Chemistry; Petrology; Mercury; Mineralogy

1. Introduction

The Manchester coal bed is one of the more important coal resources in Clay County, Kentucky, and in the six other counties highlighted in Fig. 1. Site numbers in Clay County are designated after the sample number of the whole channel sample. Bench samples are numbered consecutively after the

whole channel sample. The Manchester and its correlatives (Hance, Clintwood, Bingham, River Gem, Lily, Horse Creek, among other names) is the stratigraphically lowest coal mined extensively in Eastern Kentucky. Previously, University of Kentucky researchers investigated the petrology and palynology of the coal in the current study area and in other parts of Eastern Kentucky where the correlative coal occurs (Eble and Hower, 1995; Esterle and Ferm, 1986; Esterle et al., 1989, 1992; Hubbard et al., 2002). Aside from brief discussion of the sulfur content, Eble and Hower (1995) did not investigate the geochemistry of the coal.

* Corresponding author. Tel.: +1-859-257-0261; fax: +1-859-257-0360.

E-mail address: hower@caer.uky.edu (J.C. Hower).

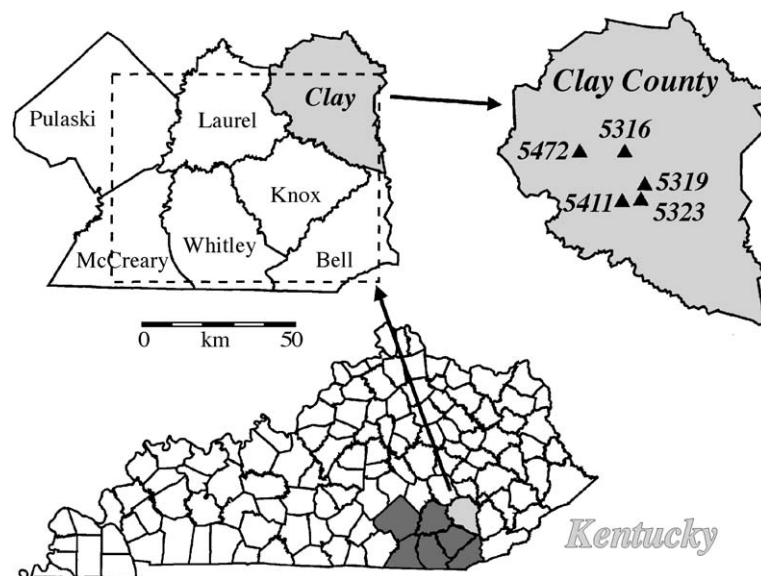


Fig. 1. Sample locations of the Manchester coal bed in Clay County, Kentucky. Dashed line on multi-county regional map indicates portion of area of vitrinite reflectance map (Fig. 2). Scale bar applies to multi-county regional map (upper left corner).

The Manchester coal bed is of Langsettian age (Eble and Hower, 1995) and marks the top of the Grundy Formation of the Breathitt Group (after Chesnut, 1996). It is overlain in much of the study area by a black shale, which contains a layer of siderite concretions about 2.5 to 5 m above the coal (Finnell, 1964).

In the current study, detailed geochemistry and mineralogy of the coal at five mine sites surrounding the town of Manchester, Clay County, Kentucky is reported (see Fig. 1). The delivery of a relatively high-Hg coal from one of the mines to a power plant prompted the investigation of the distribution of Hg and other trace elements in the coal bed profile. Parallel investigation of the distribution of Hg, and other trace elements, in fly ash at the power plant has been published elsewhere (Sakulpitakphon et al., 2000) and will be summarized here.

2. Procedure

Lithotype and whole channel coal samples were collected from a surface mine approximately 5.5 km ($37^{\circ} 09' 35''$ N/ $83^{\circ} 09' 20''$ W; Manchester 7 1/2' quadrangle (site 5472)), west of Manchester in

May 1999. The other four local sites had been sampled as part of previous investigations. Ash and whole-coal geochemistry were supplemented for this study. All regional elemental data are from a combination of sources, including the Center for Applied Energy Research and U.S. Geological Survey (Bragg et al., 1998).

For samples with numbers 5415 and lower, major oxides, reported as a percent on the ash basis, and minor elements, reported as parts per million in the ash, were determined by X-ray fluorescence on a Philips AXS II system at the Center for Applied Energy Research (CAER). Major oxides in the sample 5472–5477 sequence were analyzed by X-ray fluorescence at the CAER on a Philips PW 2404 X-ray spectrometer. XRF procedures were described by Hower and Bland (1989). Minor elements in the sample 5472–5477 sequence, with the exception of Hg and As, were analyzed via inductively coupled plasma-optical-emission spectroscopy (ICP-OES) at the CAER and are reported in parts per million in the ash. Discussion of the procedures and pitfalls in elemental analysis of coal have been presented by Huggins (2002), Carpenter (2002), and Vassilev and Tascon (2003). Mercury was analyzed at East Kentucky Power Cooperative's laboratory (Winchester,

KY) using a LECO AMA254 Advanced Mercury Analyzer, an adsorption spectrophotometer system. Arsenic was analyzed at the CAER on an inductively coupled plasma-mass spectrometer. Representative portions of each coal were subjected to oxygen-plasma (low-temperature) ashing, using an IPC 4-chamber asher unit following procedures detailed by Standards Australia (1992). The low-temperature ash (LTA) of each coal was subjected to powder XRD study using a Philips X'pert diffractometer system with $\text{CuK}\alpha$ radiation. Samples were run over an interval of 2 to 60° 2θ with a step increment of 0.02° and a counting time of 2 s per step, and the relevant data (2900 steps per sample) were stored in digital form. The minerals were identified from the diffractograms by reference to the JCPDS Powder Diffraction File. Quantitative analyses of the minerals present in each LTA were made using SIROQUANTTM, commercial interpretation software (Taylor, 1991) based on the Rietveld (1969) full-profile XRD analysis technique. Rietveld-format XRD data files were prepared using SIROQUANT for each mineral present in the samples, drawing on a comprehensive collection of crystal-structure information in the SIROQUANT database. These also incorporated information on the plane nominated within each mineral to control preferred-orientation effects, and data to allow for anomalous dispersion of the XRD beam by iron and related constituents. Details of these and other procedures are given by Ward et al. (1999) and Ward (2002) with use of functions from Matulis and Taylor (1992).

Operation of SIROQUANT involved interactive adjustment and best-fit matching of the combined XRD profiles for the individual minerals in each task file to the observed X-ray powder diffraction pattern. Overall intensities (scales) of the individual mineral phases, together with unit-cell dimensions, linewidths, and preferred orientation for the minerals, were progressively refined under operator instructions to fit the full profile of the sample's XRD pattern. Allowance was made for preferred orientation in several minerals, such as carbonates, where, although a match was obtained for the key peak positions, the distribution of peak heights was inconsistent with the standard mineral pattern. The results of the SIROQUANT analysis represent the final output from each task,

when the best possible fit had been achieved between the observed and calculated XRD patterns.

3. Discussion

3.1. Regional studies

Coal rank falls in the high volatile A bituminous range throughout the study area. Vitrinite maximum reflectance of the Manchester and overlying Blue Gem coal is shown in Fig. 2. A northward-trending deflection of the reflectance contours, with individual reflectances exceeding $0.9\% R_{\text{max}}$, disturbs the general southwest–northeast strike of the isorank contours. Hower and Rimmer (1991) noted the coincidence of this rank anomaly with the edge of a regional gravity anomaly. Other coal rank highs in eastern Kentucky also correspond to similar anomalies, leading the latter authors to speculate that basement discontinuities channeled thermal fluids through the overlying Paleozoic section, causing the rank highs. Hower et al. (1991) noted that coal rank and chlorine content are both higher on the northwest side of the Pine Mountain thrust fault (southeast of the present study area) than for correlative coals on the thrust sheet, suggesting that the emplacement of Pine Mountain may have played a role in the development of both coal rank and coal geochemistry. Collins (1993), in a statistical study of chemical

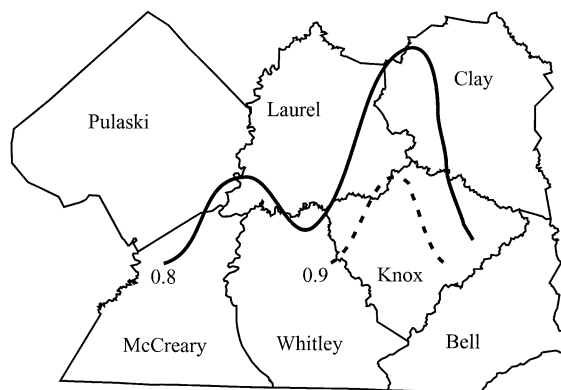


Fig. 2. Vitrinite maximum reflectance (kriged contours) of the Manchester and Blue Gem coal bed. Scale bar and axes are in feet (1 ft = 0.3045 m).

data later published by Bragg et al. (1998) (much of the data for the immediate study area, including vitrinite reflectances, had been published by Currens et al., 1987), also noted that the “brine” elements are higher in front of the Pine Mountain thrust fault than on the thrust sheet. Coal rank trends compiled by Collins (1993) from principal components analysis generally correspond to the trends noted by Hower and Rimmer (1991), except for areas where the latter researchers had access to samples not part of the U.S. Geological Survey collection (or otherwise eliminated from Collins’ data set). There is some redundancy between the two studies since the vitrinite reflectances used by Collins (1993) were generated at the CAER and were used in the study by Hower and Rimmer (1991).

Manchester chlorine levels are high in Clay and Laurel counties (Fig. 3), consistent with the overall increase to the northwest of the Pine Mountain fault. Chlorine content exceeds 0.4% at two sample sites in Clay County, including a value of 0.47% for the coal at site 5323, within the study area. Regional highs in other elements correspond, in general, to the Cl high. Data for As and Pb are plotted as examples (Figs. 4 and 5); Pb is only plotted where available from USGS analyses (after Bragg et al., 1998). High concentrations of As and Pb do not necessarily show a good correlation. Note that some samples with >1000 ppm

As have <100 ppm Pb (both on ash basis). This is not surprising since, although both elements can have associations with sulfide minerals, they are not necessarily distributed uniformly in sulfides present in coal (Ruppert et al., 1995; Hower et al., 1997). Lead, as will be noted below, may have its primary form in a selenide, not a sulfide (Hower and Robertson, 2003). Of particular interest to this study is the Hg high (Fig. 6) which occupies the same general region as the As and Pb highs.

3.2. Local area

3.2.1. Petrology

With the exception of the site added for this study (no. 5472), coal petrology (Table 1) was discussed by Eble and Hower (1995). The benches at site 5472 generally have a high vitrinite content (Fig. 1). The exception is sample 5474, a 16-cm-thick mix of, from the base of the bench, 12-cm clarain, 3.8-cm dull clarain, and 0.2-cm fusain. Despite the apparent megascopic similarities to the underlying sample 5475 (4-cm dull clarain and 14-cm clarain), inertinite- and liptinite-rich microlithotypes are more abundant in 5474. The uppermost bench, sample 5473, has a 0.3-cm-thick pyrite band, the only megascopic mineral matter in the coal, and the source of much of the 3.36% pyritic sulfur in the sample.

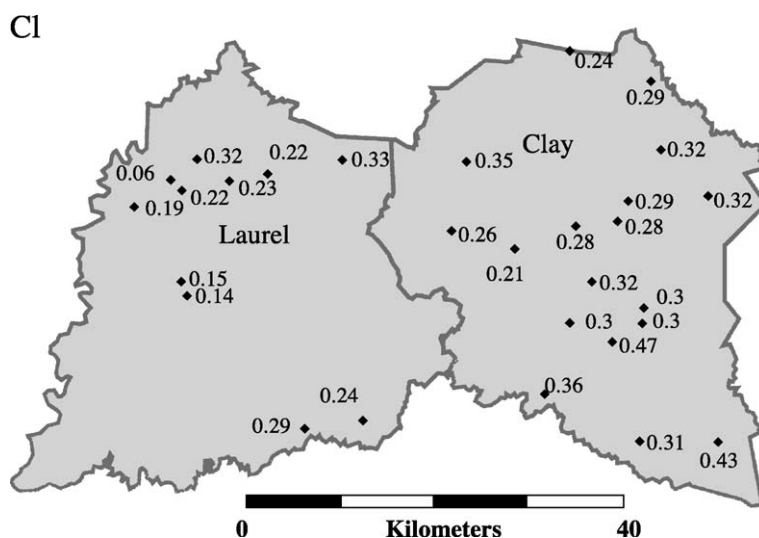


Fig. 3. Chlorine content (% , whole coal basis) of the Manchester coal bed in Clay and Laurel counties.

As

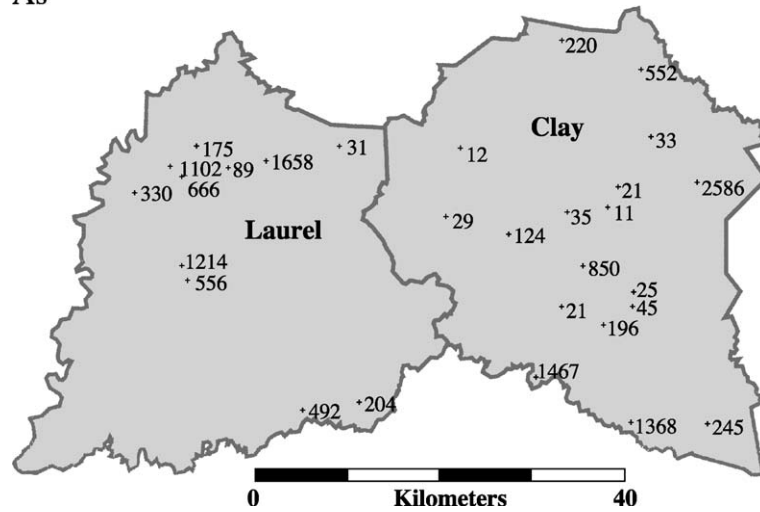


Fig. 4. Arsenic content (ppm, ash basis) of the Manchester coal bed in Clay and Laurel counties.

3.2.2. Geochemistry

The Manchester coal is generally low-sulfur in the local study area (Table 2). The exception occurs in the upper lithotypes at sites 5411 and 5472, the mine sites to the west of the town of Manchester, where high levels of pyritic sulfur elevate the total sulfur content. Sample 5473, the top lithotype at site 5472, is especially pyrite-rich, as defined by its Fe_2O_3 content (see Section 3.2.4). Trace elements

are shown in Table 3. Whole-channel As (ash basis) is higher at the two western sites, but not significantly higher than at the eastern sites. The whole-channel As is, in certain cases, among the highest found in Eastern Kentucky, comparable to high values in the Fire Clay coal bed (Hower et al., 1997).

Mercury is especially enriched in the high pyritic sulfur upper lithotypes at sites 5411 and 5472 (Figs.

Pb

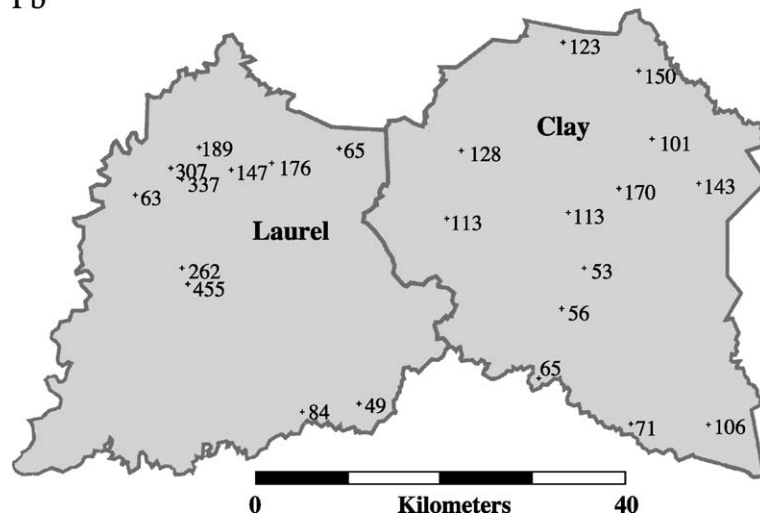


Fig. 5. Lead content (ppm, ash basis) of the Manchester coal bed in Clay and Laurel counties.

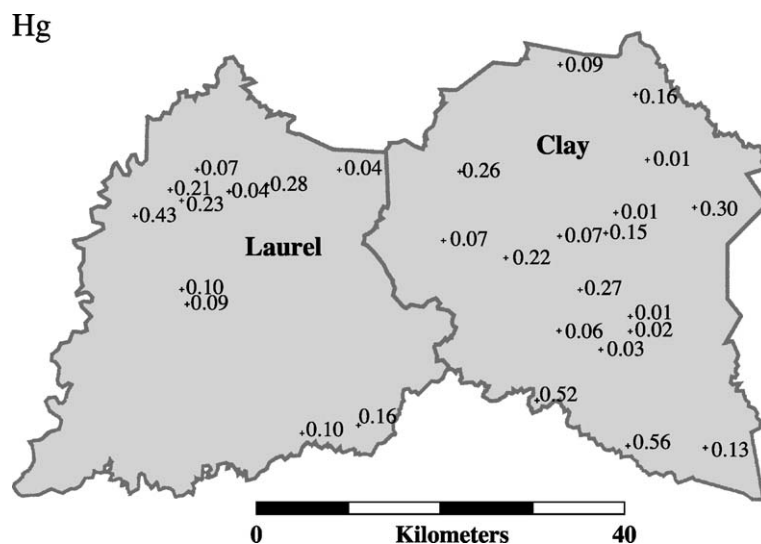


Fig. 6. Mercury content (ppm, whole coal basis) of the Manchester coal bed in Clay and Laurel counties.

7 and 8). In both cases, selective mining, eliminating the thin high-S, high-Hg upper lithotype, would have resulted in a low-S, low-Hg product, less than 0.01

ppm Hg in the case of the lower 55 cm of coal at site 5472. On-going study of the occurrence of Hg within the mineral phases indicates that the Hg is not

Table 1

Petrology of the Manchester coal bed (Vit—vitrinite; Pvt—pseudovitrinite; Fus—fusinite; Sfs—semifusinite; Mic—micrinite; Mac—macrinite; Exn—exinite; Res—resinite; $R_{\max}$ —vitrinite maximum reflectance; $R_{\max}$ s.d.— $R_{\max}$ standard deviation)

Sample	Bench	Thickness (cm)	Moisture	Ash (dry)	Vit	Pvt	Fus	Sfs	Mic	Mac	Exn	Res	$R_{\max}$	$R_{\max}$ s.d.
5316	whole coal	48.0	3.22	3.79	68.9	3.6	5.0	5.6	6.4	0.0	10.0	0.5	0.91	0.05
5317	1/2	27.4	2.77	4.84	58.4	12.8	7.4	4.5	7.3	0.4	9.0	0.2	0.84	0.04
5318	2/2	20.6	3.14	4.97	74.8	2.8	5.3	2.9	5.5	0.0	8.3	0.3	0.91	0.04
5319	whole coal	57.9	2.64	5.36	75.2	4.8	4.8	3.2	3.7	0.0	7.9	0.5	0.90	0.04
5320	1/3	16.0	2.57	10.04	75.3	2.8	5.5	4.6	2.6	0.0	9.0	0.2	0.92	0.05
5321	2/3	24.4	2.73	1.77	82.1	4.0	1.9	2.1	4.4	0.0	5.5	0.0	0.90	0.04
5322	3/3	19.6	3.10	2.41	80.6	6.4	2.6	1.9	2.7	0.0	5.7	0.1	0.92	0.03
5323	whole coal	73.2	3.03	7.11	79.3	5.5	3.1	3.0	2.9	0.0	5.9	0.3	0.93	0.05
5324	1/3	12.7	2.76	12.90	80.3	1.9	5.5	3.5	1.7	0.0	7.0	0.1	0.95	0.04
5325	2/3	26.4	2.85	1.88	82.2	3.6	2.2	2.2	3.9	0.2	5.6	0.1	0.90	0.04
5326	3/3	26.4	3.04	3.43	84.9	5.3	1.0	0.8	2.5	0.0	5.1	0.4	0.93	0.04
5411	whole coal	73.2	3.06	5.91	78.0	9.3	2.0	1.8	2.8	0.0	5.0	1.1	0.92	0.03
5412	1/4	6.4	2.57	17.60	83.9	3.1	1.5	1.0	4.2	0.0	5.9	0.4	0.88	0.05
5413	2/4	11.9	2.98	8.33	72.5	3.7	5.3	8.1	1.7	0.0	8.7	0.0	0.90	0.04
5414	3/4	38.4	3.25	1.97	80.4	5.5	3.8	2.2	3.0	0.1	4.5	0.5	0.91	0.04
5415	4/4	16.5	3.72	3.06	73.2	14.9	1.6	1.4	3.7	0.2	4.3	0.8	0.94	0.03
5472	whole coal	74.0	3.40	5.03	75.3	8.7	6.0	3.6	0.9	0.0	5.4	0.1	0.83	0.05
5473	1/5	19.0	3.09	9.28	87.9	3.0	2.3	1.7	0.1	0.1	4.8	0.1		
5474	2/5	16.0	3.78	4.32	65.8	3.7	11.0	7.7	1.8	0.2	9.8	0.0		
5475	3/5	18.0	4.32	1.49	73.9	12.5	4.7	2.6	1.3	0.0	4.9	0.1		
5476	4/5	12.0	4.13	2.13	83.1	7.3	3.2	1.8	0.2	0.0	4.3	0.1		
5477	5/5	9.0	4.38	4.65	77.3	10.0	4.1	4.1	0.3	0.0	4.1	0.1		

Table 2

Ash, sulfur, chlorine, and major oxides in the Manchester coal bed

Sample	Bench	Ash (dry)	S(t) (dry)	S(py) (dry)	S(org) (dry)	Cl	XRF (% ash)									
							MgO	Na ₂ O	Fe ₂ O ₃	TiO ₂	SiO ₂	CaO	K ₂ O	P ₂ O ₅	Al ₂ O ₃	SO ₃
5316	whole coal	3.79	0.54	0.05	0.48	0.28	1.02	0.44	3.34	1.60	56.37	1.60	2.00	0.11	31.90	0.80
5317	1/2	4.84	0.53	0.06	0.47		0.93	0.48	3.44	1.60	57.79	1.20	2.00	0.12	30.70	1.10
5318	2/2	4.97	0.53	0.06	0.46		0.98	0.11	3.69	1.70	58.58	1.20	2.10	0.11	29.60	1.20
5319	whole coal	5.36	0.75	0.10	0.65	0.30	1.30	0.63	5.57	1.60	54.31	1.20	2.30	0.11	31.20	1.00
5320	1/3	10.04	0.73	0.12	0.60		1.47	0.14	4.50	1.50	58.64	0.30	2.90	0.10	30.00	0.50
5321	2/3	1.77	0.93	0.07	0.84		1.60	2.20	12.20	0.70	30.68	9.00	1.00	0.15	30.00	11.20
5322	3/3	2.41	0.75	0.06	0.68		1.14	1.55	8.34	1.60	40.13	3.60	1.40	0.16	37.70	2.80
5323	whole coal	7.11	0.90	0.11	0.76	0.30	1.59	0.34	6.03	1.00	50.14	4.40	2.90	0.12	28.00	4.50
5324	1/3	12.90	0.88	0.20	0.67		1.54	0.07	5.21	1.30	57.63	1.40	3.30	0.12	27.80	1.20
5325	2/3	1.88	0.97	0.09	0.86		1.67	1.38	9.84	0.60	31.50	10.50	1.30	0.13	27.10	14.10
5326	3/3	3.43	0.87	0.11	0.74		1.28	0.98	8.19	1.10	36.02	8.90	1.60	0.17	30.30	9.80
5411	whole coal	5.91	1.66	0.71	0.94	0.47	1.21	0.97	21.86	1.07	42.50	2.17	2.21	0.13	24.26	1.58
5412	1/4	17.60	4.81	3.51	1.25		1.36	0.48	34.38	0.73	39.70	0.85	2.69	0.08	17.88	0.48
5413	2/4	8.33	1.02	0.32	0.69		0.78	0.69	7.57	1.77	56.68	1.29	2.16	0.10	28.32	0.77
5414	3/4	1.97	0.88	0.07	0.81		1.70	2.61	12.82	0.87	35.32	6.69	0.98	0.22	31.83	6.12
5415	4/4	3.06	0.70	0.02	0.68		0.92	1.14	5.21	1.55	44.11	3.90	1.56	0.58	36.81	2.59
5472	whole coal	5.03	1.94	0.90	1.01	0.21	0.52	0.56	33.03	1.24	36.31	1.52	1.15	0.13	21.96	0.83
5473	1/5	9.28	5.75	3.36	2.28	0.24	0.23	0.21	56.15	0.67	27.69	0.10	0.86	0.04	9.70	0.77
5474	2/5	4.32	0.58	0.02	0.55	0.24	0.70	0.59	3.48	1.71	55.39	1.30	1.35	0.17	32.24	0.50
5475	3/5	1.49	0.59	0.02	0.56	0.22	0.94	2.12	8.17	0.91	40.19	4.48	0.46	0.26	36.31	2.59
5476	4/5	2.13	0.58	0.02	0.55	0.19	0.84	1.60	5.79	2.03	43.72	3.60	0.71	0.19	37.22	1.55
5477	5/5	4.65	0.61	0.04	0.56	0.20	0.69	0.48	4.75	1.84	52.20	1.61	1.49	0.21	32.91	0.53

Table 3

Selected minor elements (ppm, ash basis) and mercury (ppm, whole coal basis)

Sample	Bench	XRF (ppm,ash)													Hg (ppm, wc)
		Mo	Zn	Cu	Ni	Co	Cr	Ba	V	Mn	Sr	Rb	Zr	As	
5316	whole coal	45	375	190	780	198	212	860	335	212	63	397	179	11	0.147
5317	1/2	42	261	160	600	108	212	790	300	203	59	377	174	5.6	0.009
5318	2/2	26	580	241	760	223	324	1220	530	315	85	430	294	12	0.028
5319	whole coal	49	480	269	283	49	179	840	255	229	82	670	205	25	0.010
5320	1/3	38	158	277	197	25	175	820	231	221	100	413	183	7	0.022
5321	2/3	43	630	530	349	42	128	860	221	258	32	2530	230		0.030
5322	3/3	52	2220	580	900	177	231	850	317	198	63	1400	250	184	0.045
5323	whole coal	28	193	216	290	53	135	640	219	237	144	900	249	45	0.018
5324	1/3	19	172	155	191	27	138	690	249	186	181	650	318	14	0.174
5325	2/3	43	449	409	347	37	104	740	184	263	52	3200	288	224	0.430
5326	3/3	29	354	467	520	102	169	600	269	198	70	1600	275	191	0.169
5411	whole coal	12	367	326	325	46	191	614	336	152	86	861	215	196	0.032
5412	1/4	0	182	279	318	28	188	467	319	141	90	322	152	134	0.375
5413	2/4	30	164	147	64	24	161	627	237	76	92	591	260	43	0.042
5414	3/4	52	770	450	340	69	146	810	279	590	40	2220	236		0.012
5415	4/4	47	790	376	800	178	314	1060	590	290	66	1530	243	10	0.014
5472	whole coal			264	438	231	305		343	277				124	0.215
5473	1/5			79	288	74	426		230	481				292	0.515
5474	2/5			236	127	65	172		430	88				8	0.009
5475	3/5			744	507	409	212		466	304					0.004
5476	4/5			863	779	981	288		556	152				12	0.002
5477	5/5			568	1368	722	326		688	202				7	0.005

Manchester coal bed: Pyritic Sulfur distribution by bench

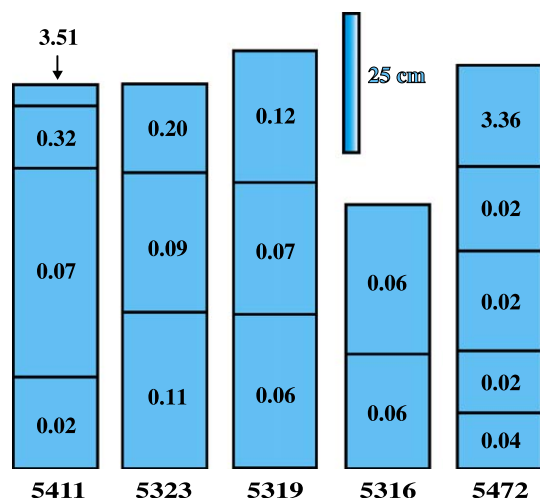


Fig. 7. Seam profiles of pyritic sulfur content by lithotype for Manchester coal bed in Clay County.

evenly distributed in the Fe-sulfides (Ruppert et al., 1995, in press).

3.2.3. Comparison to coal and ash chemistry

A comparison of the (high temperature) ash and the LTA percentages for the coals is given in Fig. 9A. The percentage of mineral matter (LTA) is about 28% higher than the percentage of high temperature ash from the same coal samples. The difference represents the loss in mass at high temperatures for minerals such as pyrite and the clay minerals.

The proportion of pyrite expected as a percentage of the LTA for each coal was calculated from the pyritic sulfur content of the coal and the LTA percentage. This calculated pyrite percentage is compared in Fig. 9B to the proportion of pyrite in the LTA as determined from X-ray diffraction using SIROQUANT. The results show a high level of agreement between the pyrite percentages indicated by the pyritic sulfur and the pyrite percentages indicated by the SIROQUANT analysis for those coals with abundant pyrite in the LTA. For coals with lower proportions of pyrite in the mineral matter, the SIROQUANT analysis seems to provide an under-estimate, relative to the chemical data. This may reflect partial oxidation of the pyrite in the plasma-

ashing process; the small proportion oxidized, if any, would be more significant where only a small proportion of pyrite is present.

The chemical composition of the coal ash implied by the quantitative analysis of the mineral matter using SIROQUANT was calculated for each coal sample, based on the proportions of each mineral indicated by SIROQUANT and stoichiometric data or typical published chemical analyses for the minerals in question. The results, after allowance for loss of H₂O, CO₂ and other constituents from the minerals during ashing, were compared to the actual ash analysis data for the same coal samples, determined using XRF techniques.

Plots illustrating the comparison for each major oxide are given in Fig. 10. These suggest a reasonable level of agreement for SiO₂, Al₂O₃, Fe₂O₃, and CaO. The differences that do occur may in part be ascribed to variation between the chemical compositions of particular minerals such as illite used in calculating the ash chemistry from SIROQUANT and the actual composition of those minerals in the coal samples. Estimates of K₂O provide a more scattered correlation (Fig. 10E), probably due to variations in the saturation of K⁺ in the coals' illite and illite/smectite constituents. MgO is also slightly under-estimated by SIROQUANT, possibly reflecting either incorporation into calcite and/or bassanite, subsequently not recognized

Manchester coal bed: Hg distribution by bench

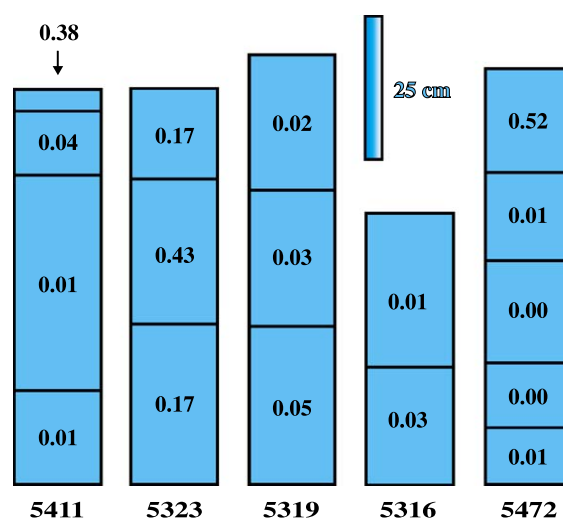


Fig. 8. Seam profiles of mercury content (ppm, whole coal basis) by lithotype for Manchester coal bed in Clay County.

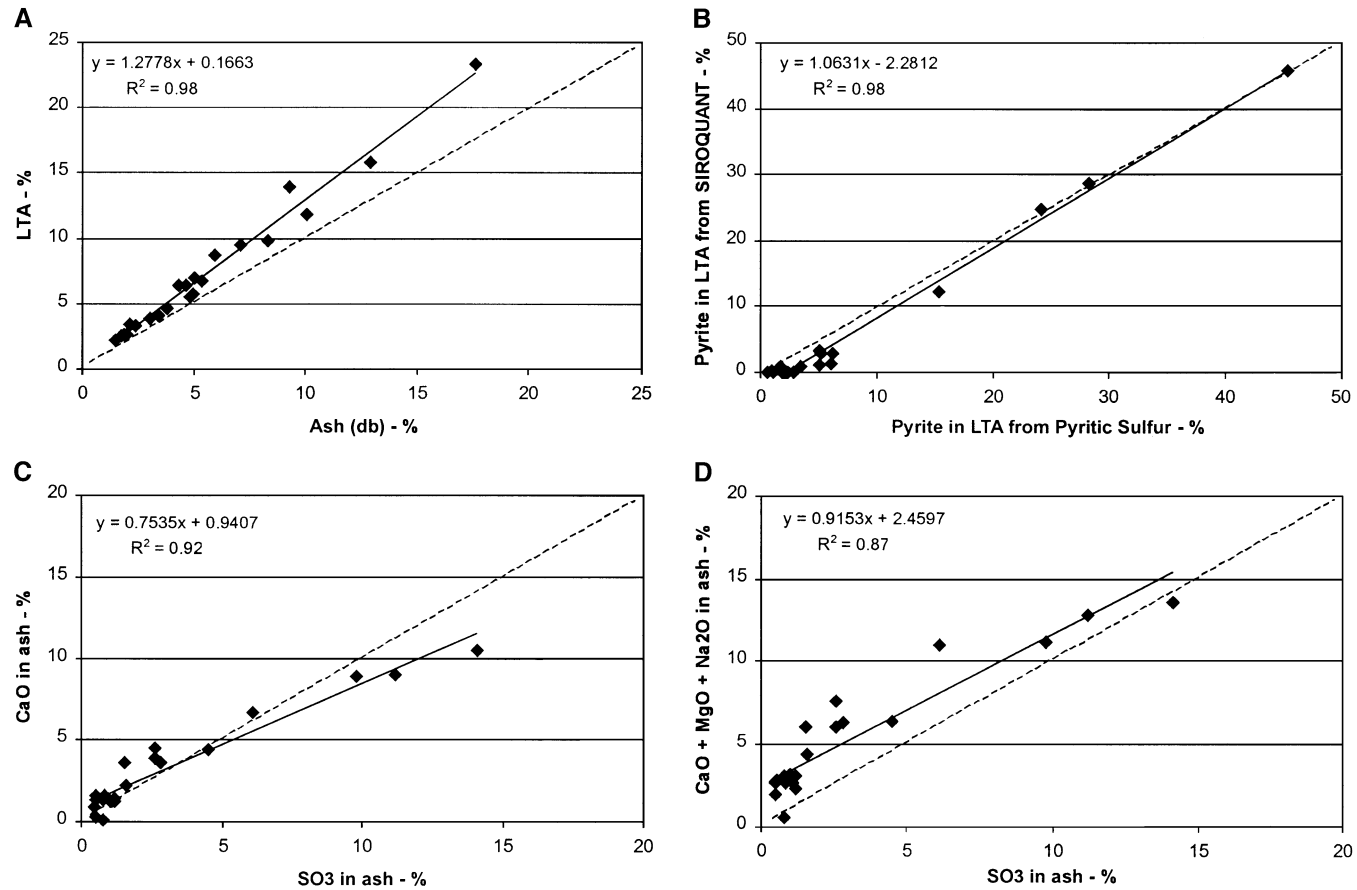


Fig. 9. (A) Comparison of ash (dry basis) vs. low-temperature ash (LTA). (B) Comparison of pyrite in LTA as estimated from pyritic sulfur vs. pyrite determined by SIROQUANT. (C) SO₃ in ash vs. CaO in ash. (D) SO₃ in ash vs. CaO + MgO + Na₂O in ash.

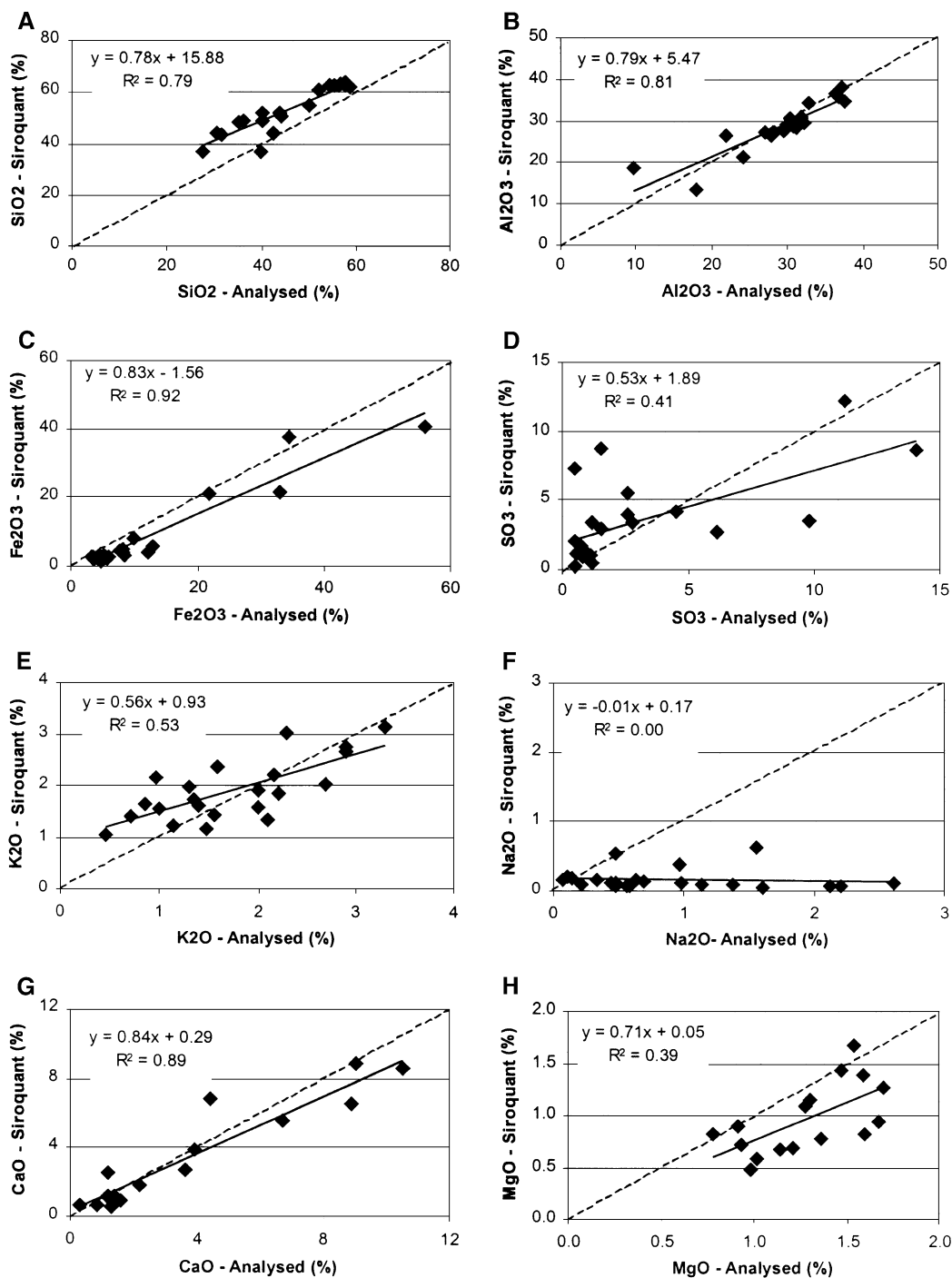


Fig. 10. Comparisons of major oxides determined by X-ray fluorescence vs. estimated percentages from SIROQUANT: (A) SiO₂; (B) Al₂O₃; (C) Fe₂O₃; (D) SO₃; (E) K₂O; (F) Na₂O; (G) CaO; (H) MgO.

by the stoichiometry, or variations within the illite structure. Na_2O does not occur in the minerals identified by XRD, and shows no particular correlation between the ash analysis and SIROQUANT values.

Although scattered, the proportion of SO_3 in the coal ash (Fig. 10D) is broadly related to the proportion of SO_3 indicated by the sulfate minerals identified in the SIROQUANT study. Better correlations exist between SO_3 and CaO in the (high temperature) ash of the coal samples (Fig. 9C).

3.2.4. Mineralogy

The mineral assemblage of the coal is dominated in most benches by well-ordered kaolinite, with minor proportions of illite and minor to trace proportions of quartz (Table 4). Irregularly interstratified illite/smectite (I/S) has also been identified separately from the XRD data, and a trace of chlorite is detected in a few samples. Pyrite occurs in trace proportions in the LTA of many of the bench samples, and is particularly abundant in the upper parts of the two westernmost seam sections (5411 and 5472).

A variable proportion of bassanite ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) is present in the LTA of most samples, especially in the lower benches of the individual coal seams. This material is an artifact of the ashing process, derived from interaction of organically associated Ca with the organic sulfur of the coal during the ashing process. Iron sulfate minerals, such as szomolnokite, jarosite, and coquimbite, also occur in the LTA in small proportions; these may have been formed by oxidation of the pyrite during ashing, or they may, like the bassanite, represent artifacts derived from reactions between organically associated elements during ashing.

The two benches of the thin northeasternmost seam section (5316) each have an essentially uniform mineralogy of well-ordered kaolinite, illite, and quartz. A small proportion of bassanite is also present, especially in the lowermost bench sample.

The other two sections from the eastern part of the area (5319 and 5323) have a very similar mineralogical profile through their bench sequence. The lowermost bench in each case is dominated by well-ordered kaolinite, with minor illite, abundant bassanite, and a very low proportion of quartz. The bench immediately above has a more poorly ordered kaolinite and only small proportions of illite and

quartz, but a relatively abundant bassanite component. The topmost bench, on the other hand, has a very well-ordered kaolinite plus more abundant quartz and illite components.

Seam section 5411 has a similar mineralogical sequence to 5319 and 5323, but has an overlying fourth bench within which almost 50% of the mineral matter consists of pyrite. The pyrite dilutes the other minerals. However, the XRD traces suggest that, if the pyrite were not present, the clay minerals and quartz would have similar characteristics and relative abundance to those of the immediately underlying bench interval. The mineral matter in the full seam section is also dominated by pyrite, due to a combination of the high LTA yield of the pyrite-bearing bench relative to the other samples studied.

Section 5472 has a similar mineralogical profile to section 5411, except for incorporation of an additional bench at the base of the seam, in which well-ordered kaolinite and abundant quartz and illite dominate the mineral matter. In view of the low quartz and illite content of the basal bench in the other sections, the basal bench in section 5472 may represent incorporation of an additional interval of coal into the seam profile.

As noted, pyrite dominates the assemblages of sulfide minerals. Minor amounts of other minerals have been found through optical and electron microscopy. As an example, small quantities of clausthalite (PbSe) have been found in sample 5473. While present in trace quantities, the mineral does demonstrate the potential complexity of the mineralization of the coals. The clausthalite has proven to be a source of Hg, containing Hg concentrations four orders of magnitude greater than in the whole coal (Hower and Robertson, 2003). Marcasite is also a source of Hg in the coal (Robertson and Hower, in preparation).

3.3. Power plant

The coal mined in Clay County (site no. 5472 is in the same mine) was shipped to East Kentucky Power Cooperative's Cooper Station Unit 1 in Pulaski County, Kentucky. The utility stockpiled sufficient coal for a 2-day burn (19–20 May 1999) of the single-mine-source Manchester coal. Coal, both raw feed and pulverized, and fly ash collection was done on 20 May 1999 at all available points. Hg analysis of the

Table 4
Mineralogy of the Manchester coal bed

Sample	Bench	LTA (ar)	Quartz	Kaolinite	Illite	Illite/ smectite	Pyrite	Szomolnokite	Coquimbite	Bassanite	Jarosite	Rutile	Anatase	Dolomite	Albite (?)	Siderite	Calcite	Chlorite
5316	whole coal	4.6	17.9	53.6	23.9	1.3	0			1.5			0.4		0.1	1.3	0	
5317	1/2	5.5	19.5	47.8	25.4	4	0			1.6		0				1.3	0.2	
5318	2/2	5.8	21.6	49.3	21.6	0.2	0			5.4		0			0.8	1	0	
5319	whole coal	6.7	14.8	36.9	38.4	8.1	0			1.8		0						
5320	1/3	11.8	15.7	36.1	41.8	1.8	0			0.4			1	0	0	0.6	0	2.7
5321	2/3	2.5	3.4	50.2	16.8	6.2	2.8		0.6	19.1	0		0	0.8		0.3	0	
5322	3/3	3.3	1.8	61.2	18.7	5.2	0.9			5.4			1.2	0.2		1.4		
5323	whole coal	9.5	10.6	34.2	35.5	4.8	0.1	0.4		6.2							5.8	2.3
5324	1/3	15.8	16.7	29	39.1	9.1	0			0.7			1.1	0	0	0.7	0.7	1.4
5325	2/3	2.7	3.5	44.8	18.8	5.4	2.8	2.6	0.8	9.1	2.6		1	1.1		1.5	5.9	
5326	3/3	4.1	3.4	47.1	23.3	8.5	1.1	0	0	4.6	1.3		1.7	0.8		2.2	6	1.4
5411	whole coal	8.7	9.5	30.3	23.8	4.4	12.3	11.9	1.1	3.6	0.2	0.1			2.1	0.8		
5412	1/4	23.3	10.1	10.2	27.1	4.9	28.8	12.6	1.2	0.8		0.9			3.3			
5413	2/4	9.8	19.5	41.7	30	4.3	1.3	2.3	0.3	0.6	0	0						
5414	3/4	2.6	2.3	48.8	24.1	6.7	3.3			4.2			2.4	1.7		2.1	4.2	
5415	4/4	3.9	2	63.6	19.5	2.2	0.2	0.4	0.5	7.9			1	0.4		0.7		1.5
5472	whole coal	7.0	10.6	45.5	13.3	3.7	24.8	0	0.6	0.8	0.2		0	0		0.4	0	
5473	1/5	13.9	6.1	24.3	18.3	3.8	45.8	0	1.2	0.5	0		0	0		0	0	
5474	2/5	6.4	18.2	51.6	16.8	8.7	0	0.2	2.1	1.5			0.2	0.2		0.2	0.2	
5475	3/5	2.2	1.6	71.8	13.6	0	0.9	0.8	0.5	4.2	1.6		1.4	0.7		1.4	1.5	
5476	4/5	3.4	1.5	73.2	10.6	7.2	0	0	0.9	3.2	1.2		0	0.5		0.5	1.3	
5477	5/5	6.4	14	65.7	18	0.4	0	0	0.2	1.6	0			0		0.2	0	

flue gas stream, either before or after the electrostatic precipitators, was not possible. The power plant study was presented in detail in the work of Sakulpitakphon et al. (2000).

The Hg content of the whole pulverized coal was 0.24 ppm, comparable to the 0.22 ppm of the whole coal at the mine site. Previous studies, both at the CAER and elsewhere (Hassett and Eylands, 1999; Hower et al., 1999, 2000a,b), have demonstrated that Hg capture by fly ash is dependant upon flue gas temperature and fly ash carbon amount and form. Specifically, potential for Hg capture on fly ash increases with a decrease in flue gas temperature, with an increase in fly ash carbon, and with an increase in carbon surface area.

In Cooper unit 1, fly ash Hg did increase with decreasing temperature of the flue gas, with the electrostatic precipitator (ESP) ashes having more Hg (0.83 ppm) than economizer (0.01 ppm) and mechanical ashes (0.35 ppm) collected at earlier, hotter portions of the gas stream. The relationship to fly ash carbon content within the ESP ashes was not as simple as previous studies would have predicted. The finer fractions (– 500 mesh, <25 μm) had greater concentrations of Hg than the higher-carbon coarser fractions. Sakulpitakphon et al. (2000) considered the possibility that the Hg distribution was complicated by disproportional contributions of thicker-walled carbons in the coarser fractions and by shielding of carbon surfaces by precipitation of low-surface area inorganic phases. Neither possibility could be proven within the context of their study. Hower et al. (2000b) did note similar complications in the relationship of Hg concentration to fly ash carbon type.

Trace elements which are readily volatilized in combustion, such as Zn, Pb, and As, are also concentrated in the ESP fly ashes, particularly in the finer fractions of the fly ash.

4. Summary

The regional picture of the Manchester coal indicates that coincident highs in the concentration of Cl, As, Pb, and Hg occur in Clay County, Kentucky. Closer examination of the coal bed reveals that while certain elements are distributed relatively evenly throughout the vertical profile, other elements, such

as arsenic at site 5472, have a distinct vertical segregation. Hg, in particular, is concentrated in the top, high-sulfur lithotype at sites 5472 and 5411, both in the western portion of the local study area. At least one other mine, a short distance (1–2 km) from site 5472, unavailable for sampling but with Hg analyses known through utility monitoring, had high Hg (0.6 ppm Hg [whole coal basis; analysis of delivered coal]).

Is the mineralization a function of epigenetic emplacement of sulfides through interaction with marine waters, or is there an additional component of diagenetic emplacement of trace elements? Certainly, the framboidal pyrite found within the high-sulfur lithotypes is likely a consequence of peat-stage, syngenetic mineralization. The coarse pyrite shows signs of multiple generations of growth, indicative of diagenetic alteration. In addition, coarser sulfides and clausthalite (Hower and Robertson, 2003) are emplaced within inertinite macerals, another indication of secondary development of minerals. Detailed studies of the distribution of trace elements, including Hg, within sulfides is on-going. Such work may shed light on the paragenesis of the mineral assemblages with respect to the metamorphism of the coal.

As noted, previous studies by Collins (1993) and Hower (Hower and Rimmer, 1991; Hower et al., 1991) suggested that emplacement of the Pine Mountain thrust fault may have accelerated fluid flow in the sediments in front (northwest) of the thrust sheet. Similarly, Garven et al. (1993) attributed the emplacement of Mississippi Valley-Type ore deposits in east Tennessee, in part, to the Pine Mountain thrusting and consequent enhanced fluid flow. Examples from other coalfields support fluid flow as a possible mechanism in coal rank enhancement (Hower and Gayer, 2002). In our study area, channeling of thermal fluids by basement discontinuities and their overlying structures may have served to elevate both the coal rank and the coal trace element content in the Manchester, and other, coals.

Selective mining, while not likely to be economic in small-scale surface mining operations such as this, could have eliminated most of the Hg and pyritic sulfur. The top 19 cm of the coal bed (5472) had 0.52 ppm Hg and 3.36% S_{py} , whereas the bottom 55 cm had <0.01 ppm Hg and 0.02% S_{py} . Of course, selective mining would transfer the waste problem to the mining operation. Sakulpitakphon et al. (2000)

demonstrated that some, but likely not all, of the Hg gets captured by the fly ash. Flue gas desulfurization, not conducted at the Cooper power plant, would also capture Hg.

Acknowledgements

Sakulpitakphon was supported by a grant from CONSOL Energy, with additional support provided by the CAER. Personnel at East Kentucky Power Cooperative's Cooper Station and central laboratory assisted in the sampling of coal and fly ash at the power plant. East Kentucky Power Cooperative's central laboratory allowed us to use analytical equipment in their facility. Ray Philpot, owner of the mine property, cooperated in sampling of coal at the mine site. We thank reviewers Hal Gluskoter and Allan Kolker, both at the U.S. Geological Survey, for their constructive comments.

References

- Bragg, L.J., Oman, J.K., Tewalt, S.J., Oman, C.L., Rega, N.H., Washington, P.M., Finkelman, R.B., 1998. U.S. Geological Survey Coal Quality (COALQUAL) database: Version 2.0. U.S. Geological Survey Open-file Report 97-134, CD-ROM.
- Carpenter, A.M., 2002. Coal quality assessment—the validity of empirical tests IEA Clean Coal Centre, London, CCC/63. 100 pp.
- Chesnut, D.R., 1996. Geologic framework for the coal-bearing rocks of the Central Appalachian Basin. *International Journal of Coal Geology* 31, 55–66.
- Collins, S.L., 1993. Statistical analysis of coal quality parameters for the Pennsylvanian System bituminous coals in Eastern Kentucky, USA (Unpublished PhD thesis). Chapel Hill, The University of North Carolina. 401 pp.
- Currens, J.C., Bragg, L.J., Hower, J.C., 1987. Analysis of coal samples from the Southwestern District, Kentucky. Kentucky Geological Survey, Series XI. Information Circular, vol. 21. 338 pp.
- Eble, C.F., Hower, J.C., 1995. Palynologic, petrographic, and geochemical characteristics of the Manchester coal bed in eastern Kentucky. *International Journal of Coal Geology* 27, 249–278.
- Esterle, J.S., Ferm, J.C., 1986. Relationship between petrographic and chemical properties and coal seam geometry, Hance seam, Breathitt Formation, southeastern Kentucky. *International Journal of Coal Geology* 6, 199–214.
- Esterle, J.S., Ferm, J.C., Tie, Y.-L., 1989. A test for the analogy of tropical domed peat deposits to “dulling up” sequences in coal beds—preliminary results. *Organic Geochemistry* 14, 333–342.
- Esterle, J.S., Gavett, K.L., Ferm, J.C., 1992. Ancient and modern environments and associated controls on sulfur and ash in coal. In: Platt, J. et al. (Eds.), *One Point Two—New Perspectives on Central Appalachian Low-Sulfur Coal Supplies*. Coal Decisions Forum Tech Books, Fairfax, VA, pp. 143–170.
- Finnell, T.L., 1964. Geology of the Manchester Quadrangle, Kentucky. U.S. Geological Survey Map GQ-318, 1:24,000 scale.
- Garven, S., Ge, S., Person, M.A., Sverjensky, D.A., 1993. Genesis of stratabound ore deposits in the midcontinent basins of North America: 1. The role of regional groundwater flow. *American Journal of Science* 293, 497–568.
- Hassett, D.J., Eylands, K.E., 1999. Mercury capture on coal combustion fly ash. *Fuel* 78, 243–248.
- Hower, J.C., Bland, A.E., 1989. Geochemistry of the pond creek coal bed, Eastern Kentucky coalfield. *International Journal of Coal Geology* 11, 205–226.
- Hower, J.C., Gayer, R.A., 2002. Mechanisms of coal metamorphism: case studies of Paleozoic coalfields. *International Journal of Coal Geology* 50, 215–245.
- Hower, J.C., Rimmer, S.M., 1991. Coal rank trends in the Central Appalachian coalfield: Virginia, West Virginia, and Kentucky. *Organic Geochemistry* 17, 161–173.
- Hower, J.C., Robertson, J.D., 2003. Clausthalite in coal. *International Journal of Coal Geology* 53, 219–225.
- Hower, J.C., Riley, J.T., Thomas, G.A., Griswold, T.B., 1991. Chlorine in Kentucky coals. *Journal of Coal Quality* 10, 152–158.
- Hower, J.C., Robertson, J.D., Wong, A.S., Eble, C.F., Ruppert, L.F., 1997. Arsenic and lead concentrations in the Pond Creek and Fire Clay coal beds, Eastern Kentucky. *Applied Geochemistry* 12, 281–289.
- Hower, J.C., Trimble, A.S., Eble, C.F., Palmer, C., Kolker, A., 1999. Characterization of fly ash from low-sulfur and high-sulfur coal sources: partitioning of carbon and trace elements with particle size. *Energy Sources* 21, 511–525.
- Hower, J.C., Finkelman, R.B., Rathbone, R.F., Goodman, J., 2000a. Intra- and inter-unit variation in fly ash petrography and mercury adsorption: examples from a Western Kentucky power station. *Energy and Fuels* 14, 212–216.
- Hower, J.C., Maroto-Valer, M.M., Taulbee, D.N., Sakulpitakphon, T., 2000b. Mercury capture by distinct fly ash carbon forms. *Energy and Fuels* 14, 224–226.
- Hubbard, T.E., Miller, T.R., Hower, J.C., Ferm, J.C., Helfrich, C.T., 2002. The upper Hance coal bed in Southeastern Kentucky: palynologic, geochemical, and petrographic evidence for environmental succession. *International Journal of Coal Geology* 49, 177–194.
- Huggins, F.E., 2002. Overview of analytical methods for inorganic constituents in coal. *International Journal of Coal Geology* 50, 169–214.
- Matulis, C.E., Taylor, J.C., 1992. Intensity calibration curves for Bragg–Brentano X-ray diffractometers. *Powder Diffraction* 7, 89–94.
- Rietveld, H.M., 1969. A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography* 2, 65–71.
- Ruppert, L.J., Hower, J.C., Eble, C.F., 1995. Arsenic in coal: using the modes of occurrence to predict behavior during combustion. 12th International Pittsburgh Coal Conference, pp. 1144–1145.

- Ruppert, L.J., Hower, J.C., Eble, C.F., 2004. Arsenic-bearing pyrite and marcasite in the fire clay coal bed, Middle Pennsylvanian Breathitt Formation, eastern Kentucky. *International Journal of Coal Geology* (in press).
- Standards Australia, 1992. Higher rank coal-mineral matter and water of constitution. Australian Standard 1038.22 (16 pp.).
- Sakulpitakphon, T., Hower, J.C., Trimble, A.S., Schram, W.H., Thomas, G.A., 2000. Mercury capture by fly ash: study of the combustion of a high-mercury coal at a utility boiler. *Energy and Fuels* 14, 727–733.
- Taylor, J.C., 1991. Computer programs for standardless quantitative analysis of minerals using the full powder diffraction profile. *Powder Diffraction* 6, 2–9.
- Ward, C.R., 2002. Analysis and significance of mineral matter in coal seams. *International Journal of Coal Geology* 50, 135–168.
- Ward, C.R., Taylor, J.C., Cohen, D.R., 1999. Quantitative mineralogy of sandstones by X-ray diffractometry and normative analysis. *Journal of Sedimentary Research* 69, 1050–1062.
- Vassilev, S.V., Tascon, J.M.D., 2003. Methods for characterization of inorganic and mineral matter in coal: a critical overview. *Energy and Fuels* 17, 271–281.